L Number	Hits	Search Text	DB	Time stamp
1	358	ARC same (plasma with etch$3)	USPAT; US-PGPUB	2002/11/15 14:03
2	68	ARC same (plasma with etch$3) same resist$3	USPAT; US-PGPUB	2002/11/15 13:28
3	41	(ARC same (plasma with etch$3) same resist$3) and @ad<=19991102	USPAT; US-PGPUB	2002/11/15 14:11
9	609	ARC and ((removing or etching) with (resist or photoresist)) same plasma	USPAT; US-PGPUB	2002/11/15 14:25
10	26	ARC same (resist or photoresist) same plasma same selectivity	USPAT; US-PGPUB	2002/11/15 14:25
11	0	ARC same (resist or photoresist) same plasma same selectivity	EPO; JPO; DERWENT; IBM_TDB	2002/11/15 14:25
12	592	(ARC and ((removing or etching) with (resist or photoresist)) same plasma) not (ARC same (resist or photoresist) same plasma same selectivity)	USPAT; US-PGPUB	2002/11/15 14:25
13	411	((ARC and ((removing or etching) with (resist or photoresist)) same plasma) not (ARC same (resist or photoresist) same plasma same selectivity)) and @ad<=19991102	USPAT; US-PGPUB	2002/11/15 15:02
14	30	(((ARC and ((removing or etching) with (resist or photoresist)) same plasma) not (ARC same (resist or photoresist) same plasma same selectivity)) and @ad<=19991102) and (ARC with (("SiON") or (silicon adj oxynitride)))	USPAT; US-PGPUB	2002/11/15 15:03

US-PAT-NO: 6291361

DOCUMENT-IDENTIFIER: US 6291361 B1

TITLE: Method and apparatus for high-resolution in-situ plasma etching of inorganic and metal films

---------- KWIC ---------

The etch rate of a **plasma** system is determined by the power supplied to the electrodes which are attached to the workpiece support 716, the gas etchant chemistry, and the vacuum level contained within the etching chamber 702. In accordance with a preferred embodiment of the present invention, fluorine and chlorine based gases are used to etch an inorganic dielectric **ARC** film. The etch **selectivity** between the **photoresist** and the inorganic dielectric **ARC** is improved by adding fluorine based chemistries such as CHF.sub.3, SF.sub.6, or other CH.sub.x F.sub.y compounds to the chlorine gas as a breakthrough process. The high etch **selectivity** between the oxide and the metal is then utilized with only chlorine based **plasma**. An example containing specific recipes evidencing this preferred embodiment of the present invention is as follows:

US-PAT-NO: 6268457

DOCUMENT-IDENTIFIER: US 6268457 B1

TITLE: Spin-on glass anti-reflective coatings for photolithography

---------- KWIC ----------

Next, a pattern is etched in the dyed SOG **ARC** layer 24 through the opening in **photoresist** layer 26 to produce the etched stack of FIG. 2f. A fluorocarbon etch, which has a high **selectivity to photoresist,** is used to etch the dyed SOG **ARC** layer 24. The response of the dyed SOG to a fluorocarbon etch provides an additional advantage of the dyed SOG over organic **ARC** layers, which require an oxygen **plasma** etch. An oxygen **plasma** etch can degrade the critical dimension of the developed **photoresist because the photoresist,** being organic based, is also etched by an oxygen **plasma**. A fluorocarbon **plasma** consumes less **photoresist** than an oxygen **plasma**. At shorter UV wavelengths, depth of focus requirements will limit the thickness of **photoresist** layer 26 at the exposure step shown in FIG. 2d. For example, it is estimated that at 193 nm, the thickness of **photoresist** layer should be approximately 300 nm. Thus, as these short wavelengths start to be employed, it will be important to have an **ARC** layer that can be etched selectively with respect to the **photoresist**.

The fluorocarbon etch is continued through the dielectric layer 22 to produce the stack of FIG. 2g. **Photoresist** layer 26 is partially consumed during the continued etch process. Finally, the **photoresist** layer 26 is stripped using an oxygen **plasma** or a hydrogen reducing chemistry and the SOG **ARC** layer 24 is stripped using either a buffered oxide etch, for example a standard hydrofluoric acid/water mixture, or an aqueous or non-aqueous organoamine.

Advantageously, the SOG **ARC** layer can be stripped with solutions that show a good **selectivity** with respect to the underlying dielectric layer. Thus, the general photolithographic method shown in FIGS. 2a-2h illustrate the process advantages of dyed SOG materials as anti-reflective coating layers.

US-PAT-NO: 6291356

DOCUMENT-IDENTIFIER: US 6291356 B1

TITLE: Method for etching silicon oxynitride and dielectric antireflection coatings

---------- KWIC ---------

The present disclosure pertains to a method for **plasma** etching a semiconductor film stack. The film stack includes at least one layer comprising silicon oxynitride. The method includes etching the silicon oxynitride-comprising layer using an etchant gas mixture comprising chlorine and at least one compound containing fluorine and carbon. The atomic ratio of fluorine to chlorine in the etchant gas ranges between about 3:1 and about 0.01:1; preferably, between about 0.5:1 and about 0.01:1; most preferably, between about 0.25:1 and about 0.1:1. The etchant gas forms a fluorine-comprising polymer or species which deposits on exposed surfaces adjacent to the silicon oxynitride-comprising layer in an amount sufficient to reduce the etch rate of an adjacent material (such as a **photoresist**) while permitting the **etching** of the silicon oxynitride-comprising layer.

The present invention pertains to a method of etching silicon oxynitride and other oxygen-containing materials. **Silicon oxynitride** is primarily used as an antireflective coating (**ARC**) and is often referred to as a "dielectric **ARC**". Silicon oxynitride is frequently used in combination with deep ultraviolet (DUV) photoresists.

In the field of semiconductor device fabrication, DUV photoresists have been developed which take advantage of shorter wavelengths of ultraviolet radiation

to enable the patterning of smaller electronic and optical devices than possible with traditional, or so called I-line, photoresists. Generally, the photoresist is applied over a stack including layers of various materials to be patterned in subsequent processing steps. Some of the layers in the stack are consumed during the process of patterning underlying layers which become part of the functioning device. To take advantage of the spacial resolution of the photoresist, it is necessary to use an antireflective coating (**ARC**) layer underlying the photoresist in order to suppress reflection off other layers in the stack during photoresist exposure. Thus, the **ARC** layer enables patterning of the photoresist to provide an accurate pattern replication.

Though the most commonly used **ARC** material is titanium nitride, a number of other materials have been suggested for use in combination with DUV photoresists. For example, U.S. Pat. No. 5,441,914, issued Aug. 15, 1995 to Taft et al., describes the use of a silicon nitride antireflective layer, while U.S. Pat. No. 5,525,542, issued Jun. 11, 1996 to Maniar et al., discloses the use of an aluminum nitride antireflective layer. U.S. Pat. No. 5,539,249, issued Jul. 23, 1996 to Roman et al., describes the use of an antireflective layer of silicon-rich silicon nitride.

Recently, there has been increased interest in the use of silicon oxynitride as an antireflective coating due to its ability to function well in combination with DUV photoresist. Silicon oxynitride typically (but not by way of limitation) has a formula of SiO.sub.x N.sub.y H.sub.z, where x ranges from 0 to about 2, y ranges from 0 to about 1, and z ranges from 0 to about 1. By changing the composition of the **silicon oxynitride ARC** layer, one can control reflection onto the photoresist during imaging of the photoresist layer. When SiO.sub.x N.sub.y H.sub.z is used as an **ARC,** x, y, and z typically range between about 0.2 and about 0.5.

Silicon oxynitride as an ARC enables efficient suppression of the reflection from underlying layers, while providing superior chemical properties which prevent an undesirable effect, known as photoresist poisoning, in photoresist patterning. Photoresist poisoning refers to reaction of the surface underlying

the photoresist with moisture to form amino basic groups (NH2.sup.-) which react with the photogenerated acid which is responsible for the photoresist development. Deactivation of the acid by the amino groups is believed to be responsible for formation of the "foot" (widening of the photoresist line just above the substrate) on some ARC mater**ial**s, such as titanium nitride.

With reference to a **silicon oxynitride** layer used as an antireflective coating, in such an application, a typical stack of materials for pattern transfer would include (from bottom to top): A substrate, which is a dielectric layer used to separate a metal interconnect layer (to be patterned on **plasma etching** of the etch stack) from underlying layers of the integrated circuit; a barrier layer, which prevents the diffusion of material between a conductive layer and the substrate; a conductive layer, which is typically aluminum or an alloy thereof, an antireflective coating (**ARC**) layer, which reduces reflection back into the **photoresist** during its exposure in the lithography step and allows for better pattern reproduction; and, a **photoresist** layer, which is imaged to provide the pattern for transfer to underlying layers.

It would then be desirable to have a dry, plasma-based etch process for transfer of the pattern from the developed photoresist through all of the layers within the complete etch stack, including an **ARC** layer, a conductive layer, and a barrier layer. Etching of a metal-comprising stack is traditionally achieved in a metal etch chamber using etch stacks with **ARC** layers such as titanium nitride. However, as silicon oxynitride is a dielectric material, its patterning is traditionally reserved for dielectric etch chambers used for etching oxide and nitride. As a result, the substrate is typically moved from one process chamber to another, which lowers the overall productivity of the whole process.

The present invention details a method permitting the etch of a dielectric-comprising **ARC** layer, such as a **silicon oxynitride ARC,** in the same chamber as is used for etching the rest of the metal-comprising stack. We have developed a plasma etch process which provides adequate selectivity for etching

a **silicon oxynitride ARC** layer over organic-based photoresists. In addition, we have obtained a good etch rate for a **silicon oxynitride ARC** layer, while providing excellent pattern transfer through the **ARC** layer and other layers of a six-layer, metal-comprising stack. Further, the method of the invention solves a series of integration problems stemming from the fact that the chemistry used for etching the **silicon oxynitride ARC** layer is very different from that used in the metal etch.

In a highly preferred embodiment of the invention, a film of silicon oxynitride is **plasma** etched, and better selectivity of **etching** is achieved relative to a film of a lower oxygen content material, such as a **photoresist**, by using a fluorine-comprising **plasma**. Preferably, the fluorine-comprising **plasma** also comprises a source of carbon. Examples of **plasma** feed gases which provide both fluorine and carbon include fluorocarbons such as CHF.sub.3, CF.sub.4, CF.sup.3 Cl, C.sub.2 F.sub.4, C.sub.2 F.sub.6, and combinations thereof. The fluorocarbon gases may be combined with other gases which increase the halogen content of the **plasma**, such as Cl.sub.2, F.sub.2, HF, HCl, NF.sub.3, or SF.sub.6, for example, but not by way of limitation. The addition of such other gases is helpful in increasing the etch rate of, and in some instances the etch selectivity toward, the silicon oxynitride. When the gas used to increase the halogen content comprises a halogen other than fluorine, such as chlorine, the etch rate of some other stack materials, such as a TiN.sub.x barrier layer, is also increased. The addition of chlorine to a fluorocarbon-containing **plasma** should enhance etch of such a barrier layer material along with the silicon oxynitride, while the etch of an oxygen-poor material such as a photoresist is suppressed.

We have discovered a preferred combination of **plasma** etch gases which provides an unexpectedly high etch rate, while providing selectivity toward **etching** the silicon oxynitride over patterning **photoresist**. The preferred etchant gas mixture includes chlorine and at least one compound comprising fluorine and carbon. The atomic ratio of fluorine to chlorine in the etchant gas mixture ranges between about 3:1 and about 0.01:1. A ratio of about 3:1

fluorine:chlorine is recommended for high silicon oxynitride to photoresist etch selectivity. It is expected that the use of CF.sub.4 rather than CHF.sub.3 would require less Cl.sub.2 to selectively etch silicon oxynitride and that CF.sub.4 alone is likely to be sufficient. Further, since the silicon etch rate is dependent on fluorine rather than chlorine, the use of CF.sub.4 should increase the etch rate of silicon oxynitride and may provide an improvement in etch selectivity as compared with CHF.sub.3.

FIG. 1 shows a schematic of the cross-sectional view of a preferred embodiment metal etch stack 100 incorporating (from top to bottom) a patterned DUV photoresist 121, a layer of **silicon oxynitride** 120 as the **ARC** layer, a second titanium nitride barrier layer 118, a second titanium wetting layer 117, an aluminum alloy layer 116, a first titanium nitride barrier layer 114, and a first titanium wetting layer 112, all deposited on a substrate 110 which comprises a layer of silicon dioxide (typically overlying a silicon wafer surface, which is not shown).

FIG. 4A shows a schematic of a cross-sectional view of a preferred embodiment metal etch stack 400 incorporating (from top to bottom) a patterned DUV photoresist 421, a layer of **silicon oxynitride** 420 as the **ARC** layer, a second titanium nitride barrier layer 418, an aluminum alloy layer 416, a first titanium nitride barrier layer 414, and a titanium wetting layer 412, all deposited on a substrate 410 comprising a layer of silicon dioxide (typically overlying a silicon wafer surface which is not shown).

We wanted to use silicon oxynitride as an anti-reflective coating in a multi-layered etch structure for the **plasma** etching of an aluminum conductive layer. To etch the silicon oxynitride, which may include an oxide capping layer, we used a fluorocarbon-comprising **plasma**. During development of the **etching** process, we discovered that we could adjust the selectivity of the etch for silicon oxynitride compared to the **photoresist** used to pattern the multi-layered etch structure (stack) by adjusting the atomic ratio of halogen (e.g., chlorine and/or fluorine) to carbon in the gases supplied to the process chamber.

To maximize the selectivity of the etch, the proper balance of carbon and fluorine in the **plasma** is achieved by adjusting the flow rates of gases injected into the processing chamber. Such adjustment is usually made by selecting from or combining several options. For example, the **plasma** feed gas which comprises fluorine and carbon is selected to have a particular carbon to fluorine atomic ratio, where the ratio is adjusted by selection from gases such as CHF.sub.3, CF.sub.4, C.sub.2 F.sub.4, C.sub.2 F.sub.6, or a combination thereof. If polymer formation is not desired, oxygen or another oxidizing agent which binds with carbon to form a volatile compound may be added to the feed gas in order to suppress the formation of polymer. Conversely, whenever polymer formation is desirable, it is preferable that oxygen not be included in the **plasma** feed gas composition. Alternatively, a gas which serves as a source of carbon, such as CO, may be included in the feed gas when it is desired to increase the polymer formation. It should be mentioned that, if **photoresist** is present in the etch chamber, its erosion during the **plasma etching** process produces considerable amounts of carbon, and the composition of the gas feed should be adjusted in accordance with the pattern density of the **photoresist**, and possibly with the type of **photoresist** used.

We have achieved a surprising increase in the etch rate of silicon oxynitride by adding an assisting halogen-comprising gas such as Cl.sub.2, F.sub.2, HF, HCl, or SF.sub.6 (preferably Cl.sub.2 and SF.sub.6) to the fluorocarbon-comprising plasma feed gases. This list of gases can be extended to include other gases which serve as a source of halogen atoms in the plasma. The benefits of using such an assisting gas are two-fold: (1) if etching of **silicon oxynitride** is carried out in a metal etch chamber (and this is desirable when the **silicon oxynitride** is used as an **ARC** layer in a metal stack), such halogen-containing gases are likely to be connected to the etch system for the purpose of metal etch; and (2) the addition of a halogen other than fluorine appears to provide additional flexibility in controlling the etch rates of other materials exposed to the plasma.

For example, the **etching** of a titanium nitride barrier layer is faster using chlorine than fluorine, and the addition of chlorine to a fluorocarbon-comprising **plasma** enhances the **etching** of this material simultaneously with the **etching** of silicon oxynitride, while the **etching** of an adjacent **photoresist** is suppressed due to the presence of polymer or halocarbon species on its surface.

The term "antireflective coating", "antireflective layer", or "**ARC**" includes materials which are applied to a surface to reduce its reflection of electromagnetic radiation.

Three sets of initial experiments were performed. First, the basic effect of etch chemistry was evaluated by **etching** unpatterned silicon oxynitride and unpatterned I-line **photoresist** wafers, and the etch rates were compared to estimate the selectivity. (The photoresist and silicon oxynitride were not simultaneously present in the **plasma.**) CHF.sub.3, Cl.sub.2, SF.sub.6, BCl.sub.3, and combinations thereof were evaluated in this experiment. The etch rates obtained are provided in Table 1, below. The etch conditions were as follows: the **plasma** source power was 1400 W; the bias power was 130 W; the process chamber pressure was 13 mTorr; the substrate support platen temperature was 45 .degree. C.; and the support platen back side helium pressure was 10 Torr, with a typical leak of 3-6 sccm. Etching was carried out for 40 seconds. This experiment indicated that CHF.sub.3 and Cl.sub.2 used together provided the most promising combination of selectivity and etch rate.

This example is for a three-step etch, in which the SiO.sub.x N.sub.y **ARC** layer is etched in Step 1, the underlying second titanium nitride and titanium layers are etched in Step 2, and the aluminum alloy layer, and underlying first titanium nitride and titanium layers are etched in Step 3. FIG. 2A illustrates the schematic cross-sectional profile of the preferred embodiment stack 200 (the same stack as 100 described with reference to FIG. 1) during the three etching steps.

This Example is for a two-step etch, in which the SiO.sub.x N.sub.y **ARC** layer and the underlying titanium nitride and titanium layers are etched in Step 1, and the aluminum layer and titanium nitride and titanium layers which underlie the aluminum layer are etched in Step 2. FIG. 3A illustrates the schematic cross-sectional profile of the preferred embodiment etch stack 300 (the same stack as 100 described with reference to FIG. 1).

When **silicon oxynitride** is used as an **ARC** layer (as in Examples One and Two), the **silicon oxynitride** is typically deposited as a thin layer, having a typical thickness within the range of about 300 .ANG. to about 600 .ANG.. Since the silicon oxynitride layer typically represents only a small fraction (within the range of about 3% to about 12%) of the total film stack thickness that is being etched, the selectivity toward etching silicon oxynitride relative to photoresist during the silicon oxynitride etch can be easily sacrificed in favor of other process considerations, without having a significant effect on the photoresist loss during the entire etch process. Considering the small loss of photoresist during silicon oxynitride etch, sacrifice of selectivity during this step is well-justified when this permits omitting a separate processing step (to etch the titanium nitride and titanium layers underlying the silicon oxynitride).

However, there are important advantages to having at least a minimal amount (i.e., at least about 1 atomic %) of a fluorine and carbon-comprising gas in the **plasma** feed gas mixture. These advantages include increased silicon oxynitride etch rate, improved selectivity toward **etching** the silicon oxynitride relative to the **photoresist,** and a vertical etch profile of the silicon oxynitride and underlying titanium nitride (if used).

In this Example, the SiO.sub.x N.sub.y **ARC** layer and the underlying titanium nitride and titanium barrier layers are etched in a single step. The aluminum layer and titanium nitride and titanium layers which underlie the aluminum layer are etched in a multi-step etch process, which typically includes at least two steps--a main etch step and an over-etch step.

In this Example, the SiO.sub.x N.sub.y **ARC** layer and an underlying titanium nitride barrier layer are etched in a single step. The aluminum layer and titanium nitride and titanium layers which underlie the aluminum layer are etched in a multi-step etch process, which typically includes at least two steps--a main etch step and an over-etch step.

In this Example, the SiO.sub.x N.sub.y **ARC** layer and the underlying titanium nitride barrier layer are etched in a single step. The aluminum layer and titanium nitride and titanium layers which underlie the aluminum layer are etched in a multi-step etch process, which typically includes at least two steps--a main etch step and an over-etch step.

US-PAT-NO: 6184142

DOCUMENT-IDENTIFIER: US 6184142 B1

TITLE: Process for low k organic dielectric film etch

---------- KWIC ---------

Because conventional etch blocking layer materials, such as **photoresist** materials, for example, are typically removed after **etching** and the characteristic of organic dielectric layer is similar to **photoresist**, these conventional spin-on organic low k materials will show limitations on process integration. The first is low resistance to O.sub.2 **plasma** that requires complicated process sequence to protect these spin-on organic films. A method to solve this problem is that after having formed low k organic dielectric film, a hardmask layer is deposited on the dielectric film that can protect the organic dielectric film from ashing damaging. However, lateral etching can not stop happening. FIGS. 1A to 1C show the steps for detailed process flow of conventional method that damaging side wall of low k organic dielectric film.

After the photoresist 20 is imaged, dry etch 40 will transfer pattern into hardmask layer 14 and low k organic dielectric layer 12, as shown in FIG. 1A. Then, **photoresist** layer 20 is stripped by O.sub.2 **plasma** and results lateral **etching** in organic dielectric layer 12 due to carbon content, as shown in FIG. 1B and FIG. 1C. Such result in dual damascene process will change etch profile, as shown in FIGS. 2A-2D. In this process, low k organic dielectric layers 12 and 13 are separated by a stop layer 16 which can stop trench etching in this layer. A cap layer 14 that can prevent moisture absorption is also like hardmask layer. After forming a photoresist layer 30, a hole pattern is transferred into photoresist layer 30 through imaging, as shown in FIG. 2A.

Then, via is formed by using dry etching cap layer 14, low k organic dielectric layer 13, stop layer 16, and low k organic dielectric layer 12, as shown in FIG. 2B. Next, photoresist 30 is removed by using O.sub.2 **plasma** and low k organic dielectric layers 12 and 13 are etched laterally, as shown in FIG. 2C. The following is trench etch and will cause the poor profile in FIG. 2D.

Due to high carbon content (>30%) in these spin-on organic low k films, another conventional method that requires multiple films as hardmask layer to avoid direct exposure of low k film to O.sub.2 plasma is disclosed in FIGS. 3A-3G. First, a composite insulation layer comprising of low k organic dielectric film 12, SiO.sub.2 film 17 and **SiON ARC** film 18 is deposited on a substrate 10. Photoresist 30 is formed on the SiON layer 18 and imaged. SiON layer 18 is etched by using dry etch 40, as shown in FIG. 3A. Then photoresist 30 is stripped while low k film 12 can prevent from O.sub.2 plasma damage due to SiO.sub.2 layer 17; then SiO.sub.2 layer 17 is etched using SiON layer 16 as etch hardmask, as shown in FIG. 3B. Next, low k organic dielectric film 13, SiO.sub.2 layer 15, and SiON layer 14 is deposited in sequence and then another photoresist layer 31 is deposited with imaged, as shown in FIG. 3C. As the same steps from FIG. 3A to 3B, SiON layer 14 is etched using photoresist layer 31 as a mask, as shown in FIG. 3D. Then, photoresist layer 31 is stripped with avoiding O.sub.2 plasma damage on low k film 13 for the same reason mentioned above; then, SiO.sub.2 layer 15 is etched using SiON layer 14 as etch hardmask, as shown in FIG. 3E. Then, dual damascene structure is formed by using anisotropically etching low k organic dielectric films 13 and 12, as shown in FIG. 3F. Cross section of dual damascene structure is formed after metal barrier layer and metal layer deposition in sequence and etching excess metal by using chemical mechanical polishing method. However, this method has intricate steps in dual damascene technology.

The stop layer 114 is an etch barrier film such as silicon nitride (SiN) to prevent the upper trench patterns of dual damascene from being etched through if the low k organic dielectric layer 112 underlying the stop layer 116 is for via or contact. Other barrier layer may be used such as **silicon oxynitride (SiON)** as long as it has different etch characteristics than low k organic

dielectric film and can be used as **ARC** layer. That is, stop layer 114 allows a selective etch process with respect to different underlying materials and also eliminates reflection of incident light. The material and characteristics of cap layer 114 is the same in FIG. 5A.